

# PATENT SPECIFICATION

(11) 1 532 072

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- (21) Application No. 11127/76 (22) Filed 19 March 1976  
 (31) Convention Application No. 2 513 251  
 (32) Filed 26 March 1975 in  
 (33) Fed. Rep. of Germany (DE)  
 (44) Complete Specification published 15 Nov. 1978  
 (51) INT CL<sup>1</sup> D01F 8/08  
 (52) Index at acceptance  
 BSB 200 350 35Y 38Y 400 436 714 720 724 725 72Y  
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## (54) BIFILAR ACRYLIC FIBRES

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to bifilar acrylic fibres.

In particular, this invention relates to acrylic fibres and filaments with a permanent crimp, and to a process for their production.

15 There are already numerous processes for the production and application of crimped acrylic fibres. Mechanically applied crimps generally have the disadvantage that they are not permanent. There are also processes for the conjugated spinning of two or more different materials to form bicomponent or multicomponent fibres in which the individual components are present in an eccentric arrangement relative to one another in the cross-section. In cases where acrylic fibres are used, the co-spun fibres have hitherto generally been produced from at least two solutions of at least two different polymers or polymer mixtures (German Auslegeschrift No. 1,494,677). Unfortunately, this procedure has the disadvantage not only that the polymers used have to be carefully selected, but also by the further disadvantage that two different polymer solutions have to be prepared. In addition, it is known from Germany Auslegeschrift No. 1,210,123 that bifilar filaments can be produced by spinning two solutions of the same polymer, but with different concentrations the differences in concentration being said to amount to at least 4% and preferably 10%. This process is still attended by the disadvantage that two different solutions have to be prepared for subsequent conjugate spinning.

Accordingly, we have sought to produce

bicomponent fibres or filaments of a polymer with a permanent water-resistant crimp from a single solution of that polymer.

It has now surprisingly been found that bifilar filaments with excellent crimping properties can be obtained by dividing up the solution of a polymer, heating the resulting two solutions to different temperatures and then spinning them by a conventional bifilar spinning operation.

Accordingly, the present invention provides a process for the production of bifilar fibres and filaments of an acrylonitrile polymer, wherein a solution is prepared from an acrylonitrile polymer, the resulting solution is divided up into two component solutions which are subjected to bifilar spinning at different temperatures, and the filaments thus obtained are recovered. The filaments may be after-treated by standard methods, preferably the filaments are washed, stretched, optionally mechanically crimped, heat-treated and dried and optionally cut into fibres.

The polymer used is generally a copolymer which contains at least 50% by weight of acrylonitrile and up to 50% by weight of one or more ethylenically unsaturated monomers copolymerisable with acrylonitrile or a mixture of two or more of the above-mentioned polymers. However, it is particularly preferred to use polymers which contain at least 85% by weight of acrylonitrile. Comonomers suitable for use in accordance with the invention are the comonomers known in this art of the type described, for example, in U.S. Patent Specification No. 3,035,031. Particularly preferred comonomers are acrylic acid or methacrylic acid esters for example, methyl acrylate and ethyl acrylate, vinyl esters, for example, vinyl acetate, and comonomers which increase affinity for dyes, for example allyl and methallyl sulphonic acid, styrene sulphonic acid and their salts.

The solutions may be dry spun or wet

5 spun, preferably dry spun, by any of the known processes in such a way that substantially equal parts of the two components are present in the filament. In order to optimise the permanent crimp, it is best for the ratio of the polymer components in the filament to differ from 1:1, although it should not exceed a ratio of about 1:3.

10 The temperature difference between the two solution streams which is required for obtaining a particularly good crimp is of course governed by the physical and chemical properties of the polymer used, by the absolute level of the particular temperature selected and by the selected concentration of the solution. In order to determine this temperature difference, it is advisable to carry out a corresponding small-scale test in each individual case.

20 Temperature difference of about 30°C have proved to be adequate. However, larger temperature differences, for example in the range of from 40 to 120°C, are particularly preferred, the average absolute temperatures being of the order normally encountered in this art.

30 In principle, it is possible to divide the solution stream into two solution components and to establish the requisite temperature difference at any given point in front of the orifice of the spinneret. However, it is particularly favourable to carry out these measures as near to the orifice of the spinneret as possible because it is possible in this way to eliminate the need for a double pipe system for the solution stream.

40 One simple way of enhancing the crimp effect is to add small quantities of a solvent, preferably the spinning solvent, to one of the component solution streams. In the context of the invention, "small quantities" of a solvent are amounts which do not increase the difference in concentration between the solutions to beyond 4%. The solvents used are those well-known in the art of spinning acrylonitrile polymers. Preferably, dimethyl formamide, dimethyl acetamide, dimethyl sulphoxide and butyrolactone are used.

50 The two fibre components are spun by known methods in such a way that they are present in an eccentric arrangement to one another in the resulting bicomponent filament. This eccentric arrangement may be a core/cover arrangement, although it is preferably a side-by-side arrangement.

60 The bicomponent fibres are then preferably after-treated by the methods normally adopted for acrylic fibres.

65 Once it has been developed, the crimp is permanent and, for the fibres, represents the condition of minimal energy. The crimp is also permanent and elastic when

subjected to deformation. If the crimp is pulled out by mechanical deformation even to the point where the fibre breaks, it springs back into the fibre after a heat treatment.

70 The number of crimp arcs per unit length is governed by the composition of the polymer by the spinning conditions and by the type of aftertreatment. The crimp is a typical bifilar crimp, of the type also known from multicomponent fibres, i.e. it is *inter alia* helical. With numerous textiles, optimum appearance, good feel and high volume are obtained when the fibres contain from 4 to 12 crimp arcs per centimetre for a denier per filament of a 3.3 dtex.

80 The fibres are crimped by being subjected after stretching to a relaxing atmosphere at a higher temperature.

85 The invention is illustrated by the following Examples, in which parts and percentages are based on weight unless otherwise stated.

#### EXAMPLE 1.

90 An acrylonitrile copolymer of 93.6% of acrylonitrile, 5.7% of methacrylate and 0.7% of sodium methallyl sulphonate was dissolved in dimethyl formamide at 90°C. A solution with a polymer content of 29.5% was prepared. The solution was delivered to a bifilar spinneret. The solution stream was divided into two components. One of the two solution components (A) was heated to 130°C and the other (B) cooled to 40°C. The solutions had a ball drop time of 24 seconds (A) and 300 seconds (B). (The ball-drop time is a measure of solution viscosity. It is the time which a ball with a diameter of 1/8th inch ( $\approx 3.175$  mm) takes to travel a distance of 7 cm in the solution at the temperature indicated).

100 The solutions were introduced into a bifilar spinneret in a ratio of A to B of 1.2:1 and were spun side-by-side. Several bifilar spinnerets were arranged on a die base and air which had been heated to 380°C flowed past the base. The filaments were run off at a rate of 300 m/minute. The duct situated below the spinneret had a wall temperature of 170°C. After spinning, the spun material was washed with water for 30 seconds at 100°C. The material was then stretched 1:4 in water at 100°C. The filaments were then dried for 2 minutes at 100°C in the absence of tension. The resulting crimp in the filaments was intensified by boiling the filaments for 10 minutes in water, followed by tempering for 20 minutes at 130°C. The fibres had a denier of 3.3 dtex and contained 4 crimp arcs per centimetre. The number of crimp arcs per centimetre is derived from the quotient of the number of crimp arcs and the length of the fibre from which the

crimp has been just pulled out by elongation.

Spinning and aftertreatment under the same conditions as just described, but with the stretching ratio altered to 1:2.5, produced a fibre with a denier of 5.8 dtex and 10 crimps per centimetre.

#### EXAMPLE 2.

A solution in dimethyl formamide with a polymer content of 31% was prepared from an acrylonitrile polymer with the same chemical composition as described in Example 1. The solution stream was divided into two component streams A and B on its way to the bifilar spinneret. DMF was introduced into component stream B before a static mixer in such a quantity that, after the static mixer, solution B had a uniform polymer content of 27%. A solution stream A was then heated to 130°C whilst solution stream B was cooled to 40°C. Solution A had a ball drop time of 440 seconds and solution B a ball drop time of 13 seconds. The solutions were spun against one another under the same conditions as in Example 1 in a ratio of A to B of 1.3:1. The filaments thus obtained were aftertreated in the same way as in Example 1. They contained 9 crimp arcs per centimetre for a stretching ratio of 1:2.5 and 7 crimp arcs per centimetre for a stretching ratio of 1:4.

#### EXAMPLE 3.

Following the procedure of Examples 1 and 2, solutions were prepared from the same polymer. As in the preceding Examples, these solutions were divided into

components A and B and spun against one another with and without additions of DMF. The filaments were aftertreated in the same way as described in Example 1. Table 1 shows the concentrations of the two solution streams A and B, the solution temperatures, the quantitative ratio between the solutions, the solution viscosities and the number of crimp arcs per cm for the material which was stretched in ratios of 2.5 and 1:4.

#### EXAMPLE 4.

An acrylonitrile polymer mixture was prepared from two polymers x and y, of which polymer x had been completely polymerised from acrylonitrile and polymer y from 91% of acrylonitrile, 3.4% of sodium methallyl sulphonate and 5.6% of methylacrylate. The polymers x and y were present in the mixture in a ratio of 85:15. This mixture was dissolved in dimethyl formamide at 90°C. A solution with a polymer content of 25.5% was prepared. The solution was delivered to a bifilar spinneret. The solution stream was divided into two component streams A and B. The component streams were heated to different temperatures and were introduced in different quantities into the bifilar spinneret. The spinning and aftertreatment conditions for the filaments were the same as in Example 1. Table 2 shows the temperatures, the quantitative ratios and viscosities of the solution streams A and B and the number of crimp arcs per centimetre for stretching ratios of 1:2.5 and 1:4.

TABLE 1

Test No.	Polymer content of the solutions		Temperatures of the solutions before entering the spinneret		Ratio of solutions		Ball drop times (in seconds)		Crimp arcs per cm after stretching	
	A	B	A	B	A	B	A	B	1:2.5	1:4
3(i)	29.5%	29.5%	130°C	40°C	1.2	1.0	24	300	10	4
3(ii)	31 %	27.0%	40°C	130°C	1.3	1.0	440	13	9	7
3(iii)	29.5%	29.5%	130°C	40°C	1.0	1.62	24	300	7	4
3(iv)	29.5%	24.3%	130°C	80°C	1.0	1.21	24	36	7	3
3(v)*	29.5%	24.3%	130°C	130°C	1.0	1.0	24	8.5	4	2
3(vi)	31.0%	27.0%	40°C	130°C	1.04	1.0	440	13	10	5
3(vii)	31.0%	27.0%	40°C	130°C	1.0	1.0	440	13	9	5

Note:

\*Test 3(v), where the temperatures of the two solutions A and B is the same, is for the purpose of comparison.

TABLE 2

Test No.	Temperatures of the solutions		Ratio of Solutions		Ball drop times (in seconds)		Crimp arcs per cm after stretching	
	A	B	A	B	A	B	1:2.5	1:4
4(i)	130°C	70°C	1.0	1.0	26	130	5	11
4(ii)*	130°C	130°C	1.0	1.2	26	26	—	—
4(iii)	130°C	70°C	1.0	1.2	26	130	2	5

Note:

\*Test 4(ii) where the temperature of the solutions A and B is the same is for the purposes of comparison.

The Tests set out in Tables 1 and 2 above show that the crimp depends not only on the temperature difference between the two solutions but also on the ratio of the two solutions.

The dependency of the crimp on the ratio of the two solutions is illustrated by comparing Test 4(i) with Test 4(iii).

**WHAT WE CLAIM IS:—**

1. A process for the production of bifilar fibres and filaments, wherein a solution is prepared from an acrylonitrile polymer, the resulting solution is divided up into two component solutions which are subjected to bifilar spinning at different temperatures and the resulting bifilar filaments thus obtained are recovered.

2. A process as claimed in Claim 1, wherein the acrylonitrile polymer is a copolymer of at least 50% by weight of acrylonitrile and up to 50% by weight of at least one ethylenically unsaturated monomer copolymerisable with acrylonitrile.

3. A process as claimed in Claim 1 or 2, wherein the copolymer contains at least 85% by weight of acrylonitrile.

4. A process as claimed in any of Claims 1 to 3, wherein the copolymer contains at least one comonomer selected from methyl acrylate, vinyl acetate, sodium methallyl sulphonate and sodium styrene sulphonate.

5. A process as claimed in any of Claims 1 to 4, wherein the two component solutions are subjected to bifilar spinning in different quantities relative one to the other.

6. A process as claimed in Claim 5

wherein the ratio between the quantities of the polymer components of the two component solutions is in the range of from more than 1:1 up to 1:3.

7. A process as claimed in any of Claims 1 to 6, wherein a "small quantity" as herein defined of an additional solvent is added to one of the component solutions.

8. A process as claimed in any of Claims 1 to 7, wherein the filaments are dry spun.

9. A process as claimed in any of Claims 1 to 8, wherein a molecular orientation is imparted to the filaments or fibres by stretching.

10. A process as claimed in any of Claims 1 to 9, wherein the two components are spun in a side-by-side arrangement.

11. A process as claimed in any of Claims 1 to 9, wherein the two components are spun in a core/cover arrangement.

12. A process as claimed in any of Claims 1 to 11, wherein the difference between the temperature of one component solution and the other is from 40 to 120°C.

13. A process for the production of bifilar fibres and filaments substantially as herein described with reference to any of the specific Examples.

14. Fibres and filaments when prepared by a process claimed in any of claims 1 to 13.

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